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Välisalo, Tero

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RESEARCH REPORT

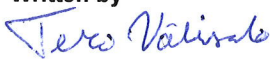


VTT-R-00066-19



Firefighting in case of Li-Ion battery fire in underground conditions: literature study

Authors: Tero Välisalo

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Summary <p>The goal of this literature study is to clarify according to the available literature how the firefighters should operate in case a Li-Ion battery-powered work machine catches fire in underground conditions, e.g. in a mine. Another goal is to find ideas and topics for further research to promote fire safety of battery-powered work machines.</p> <p>Battery powered electrical drives are nowadays been designed also for underground mining applications. Lithium-ion based rechargeable batteries are common also in heavy work machine applications. They are relatively safe, as there is no lithium metal present in the battery structure. However, Li-ion batteries can reach a self-heating stage that can lead to thermal runaway. All needed components of fire are present in the li-ion cell: fuel, heat and oxygen.</p> <p>Lithium-ion battery fire suppression is generally recommended to be accomplished mainly with lots of pure water or water-based extinguishing foam. In underground solutions, it is not an ideal option to allow the battery pack burn to self-extinguishment because of the rock integrity decreases due to heat and because of the loss of production as the underground operations should be stopped in the case of battery fire. There were no indications in any emergency guides or research papers that there might be danger of electrical shock for the firefighters while the battery pack is extinguished with water.</p> <p>To ease the work of the first responders, machine type specific instructions should be prepared. The conventional personal protective equipment used by rescue personnel in ICE car fires should be effective enough also in the case of EV battery fire, although the subject should be studied more further.</p>		
Confidentiality	Public	
Tampere 25.1.2019 <div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> Written by  Tero Välisalo research scientist </div> <div style="width: 30%;"> Reviewed by  Toni Ahonen senior scientist </div> <div style="width: 30%;"> Accepted by  Eila Lehmus research team leader </div> </div>		
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1. Introduction

Battery powered electrical drives are nowadays designed also for underground mining applications. The electrical drives produce less air pollution and therefore it decreases the ventilation power consumption in a mine. Electricity is also a lot cheaper “fuel” for mining machinery and it is assumed that the electrical machines are more reliable than the diesel-powered machines due to more simple structure and reduced number of parts.

Lithium-ion based rechargeable batteries are common also in heavy work machine applications. They are relatively safe, as there is no primary lithium (lithium metal) present in the battery structure. In lithium-ion cells there are several anode and cathode materials used (Table 1):

Table 1. Common cathode and anode materials used in lithium-ion cells (adapted from article by Nitta et.al.2015¹)

<i>Cathodes</i>	<i>Anodes</i>
LCO (LiCoO_2)	Graphitic carbons
NCA ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$)	Hard carbons
NMC ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$)	Carbon + alloying materials (e.g. Si, Sn, Ge)
LMO (LiMnO_2)	Lithium titanate, LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$)
LFP (LiFePO_4)	

Lithium oxides, which are not flammable, are used as cathode materials (e.g. LiCoO_2). However, there are still flammable parts in Li-Ion cells: the electrolyte consists of lithium salt (e.g. LiPF_6) which is dissolved to organic solvent like methylcarbonate or diethylcarbonate. The anodes are most commonly made out of carbon-based, inflammable materials². The separator, which prevents the anode-cathode contact but lets the Li-ions go through, is usually made out of plastic (polyethylene (PE) or polypropylene (PP)), which is also combustible material. Today most of the heavy duty work machine Li-ion batteries are made out of cells where the anode is made out of lithium titanate (LTO). Cells with LTO anodes are inherently safer than the other li-ion battery types as the anode is free of carbon and they will not generate any metallic lithium even if the state of charge (SOC) is below the specified level.

Li-ion batteries can reach a self-heating stage that can lead to thermal runaway. All needed components of fire are present in the li-ion cell: fuel, heat and oxygen. Some factors and conditions leading to thermal runaway are presented in Figure 1.

¹ Nitta, N., Wu, F., Lee, J.T & Yushin, G. 2015. Li-ion battery materials: present and future. *Materials Today*, vol.18, 5/2015. pp. 252-264. Elsevier.

² Lisbona, D. & Snee, T. 2011. A review of hazards associated with primary lithium and lithium-ion batteries. *Process Safety and Environmental Protection* 89. pp. 434–442. Elsevier.

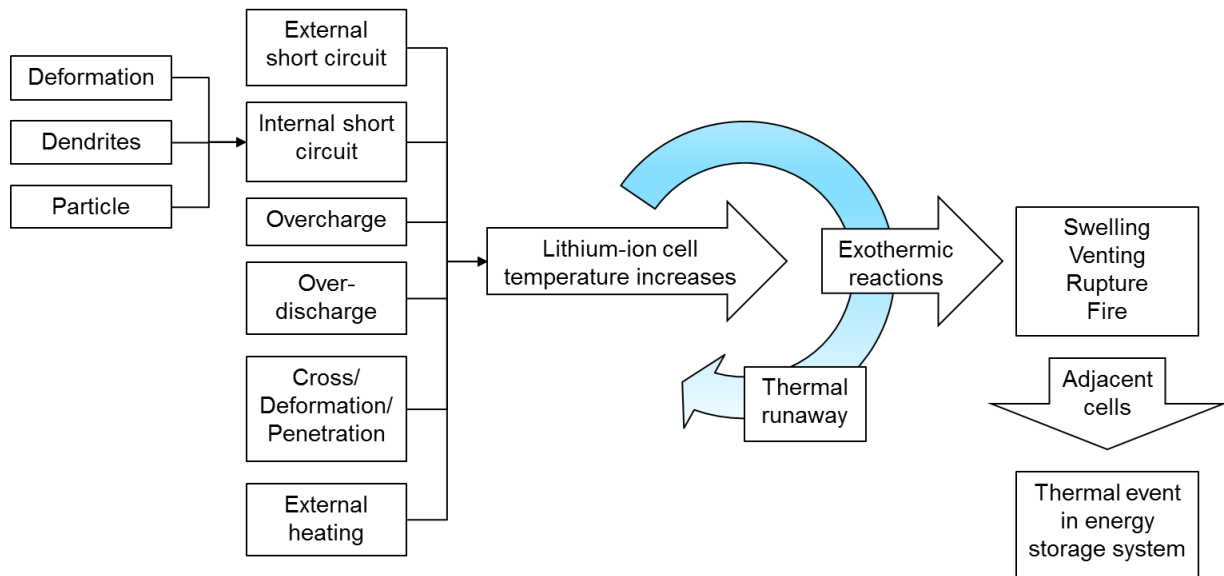


Figure 1. Potential chain of events from li-ion cell level to energy storage system level.³

2. Goal and limitations

The goal of this literature study is to clarify according to the available literature how the firefighters should operate in case a Li-Ion battery-powered work machine catches fire in underground conditions, e.g. in a mine. Another goal is to find ideas and topics for further research to promote fire safety of battery-powered work machines.

The study focuses on rechargeable lithium-ion batteries and fire incidents where li-ion batteries are involved. Safety hazards and firefighting tactics of non-rechargeable lithium batteries are not reviewed.

The study is limited to the referred literature only.

3. Methods

The literature used in this study were gathered with common search engines in the internet (Google, Bing) and the eKnowledge Search services provided by VTT information solutions department.

³ Adapted from: Andersson et.al. 2017. Safe introduction of battery propulsion at sea. SP Rapport 2017:34. RISE Research Institutes of Sweden. ISSN: 0284-5172. Available at: <https://www.diva-portal.org/smash/get/diva2:1118026/FULLTEXT01.pdf>

4. Lithium-ion battery fires

4.1 Typical lithium-ion battery fire hazards

Lisbona & Snee have published a review article in 2011: *A review of hazards associated with primary lithium and lithium-ion batteries*⁴. In their article, it was noted that in lithium-ion cells lithium metal is not re-deposited upon charging under normal circumstances and therefore they are considered safer than in primary lithium cells. The hazards associated with rechargeable lithium-ion cells can start from the following side reactions:

- Molten lithium can form in the event of overcharging. This not likely to occur in lithium-ion cells as metal lithium is replaced by lithiated carbon materials.
- Reactions between the organic solutions and the electrode surface occur when the temperature of the cell increases, particularly if the solid-electrolyte interface becomes unstable. This happens when the cell temperature rises above 70–100 °C and decomposes exothermically.
- Heat generation and thermal management are critically important for the safe operation of lithium-ion cells. Both reversible and irreversible heat generation must be considered in the battery management system. Internal resistance is responsible for irreversible heat and reversible heat is linked to the reduction reaction that takes place in the positive electrode and the heat generated at the negative electrode.

Faults and misuse during operation can cause internal and external short-circuits, overcharge, overdischarge or overheating which can result in thermal runaway, over-pressurisation, venting, fire and/or explosion of battery packs.

Thermal runaway and heat effects in lithium-ion cells are sensitive to the state of charge (the higher the charged voltage the lower the onset temperature) and depend on the history of the cell and the load applied. Thermal runaway of lithium-ion batteries is a three-stage process:

1. Anodic reactions start at about 90°C. As temperature rises above 120°C, decomposition of the solid electrolyte interface layer follows, leading to reduction of the electrolyte at the lithiated graphite negative electrode.
2. The thermal runaway mechanism, exothermic reactions at the positive electrode start as the temperature rises over 140°C. Oxygen rapidly evolves at this stage.
3. The positive electrode decomposes and the electrolyte gets oxidised at temperatures above 180°C. This is an exothermic process with a temperature rise as high as 100°C per minute.

There are several control mechanisms to protect the batteries against hazardous effects:

- At battery hardware level, safety mechanisms involve cell design features such as safety vents, shutdown additives, current cut-off device and separator materials.
- At system hardware level, electronic control to prevent overcharge, over discharge and overheating of the battery packs is necessary, including balancing to prevent unbalanced states of charge among packs.

⁴ Lisbona, D. & Snee, T. 2011. A review of hazards associated with primary lithium and lithium-ion batteries. *Process Safety and Environmental Protection* 89. pp. 434–442. Elsevier.

- The electrical hardware is essential to provide safety at system level. Fuses are needed to protect against high current excursions in the system performance, and contactors minimise the possibility of external short-circuit.
- Batteries must be provided with structural protection as well as a thermal management system (e.g. adequate ventilation) to prevent overheating due to operation or heat input from the surroundings. Thermal management of the group of cells forming the pack and module is necessary to prevent propagation of these thermal effects.

Safe operation of battery systems requires also controls at the software system level. Measurement of the battery performance is necessary to ensure safe operation. Good indicators of cell performance are battery cell/pack voltage, temperature, current and state of charge.

4.2 The combustion behaviour of large scale lithium-titanate battery

In Hefei, China, a research team tested on 2014 the combustion behaviour of large-scale lithium battery⁵. Three 50 Ah lithium-titanate batteries ($\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$) were heated with electric heater to fire. When the battery temperature exceeds a certain value, series of reactions would occur:

- breakdown of solid-electrolyte interphase for carbon based anode,
- melting of separator,
- reaction between the negative material and electrolyte,
- decomposition of electrolyte,
- reaction between positive material and electrolyte etc.

The cathode materials in the Li-ion batteries are thermally unstable to induce autocatalytic reaction with the electrolytes and generate oxygen at elevated temperature. It was also found in the tests that the charged batteries are more hazardous than uncharged ones.

The combustion process was divided into three stages:

1. **Igniting:** The pressure-limiting valve ruptured and gases rushed out from it. The flammable gases were ignited by the high temperature on electric heater and formed a jet fire. Lithium atoms react with the organic solvent in electrolyte and release abundant alkane olefin gases like C_2H_4 , C_3H_6 , C_2H_6 . The battery with higher state of charge (SOC) has a longer combustion flame after ruptured and ignited. Furthermore, with the higher SOC, the time needed to rupture and ignite is declining, which indicates the degree and velocity of inner reactions are directly depending on the SOC.
2. **Stable combusting:** In this stage, the battery combustion becomes stable and flame range changes slowly (0 % and 50 % SOC). Strong reactions occurred at this time inner the full charged battery, which led to the combustion of 100% SOC battery became more complicated and difficult to be predicted.
3. **Extinguishing:** The flame region was reduced gradually and extinguished at the end. The combustion times were about 2160 s and 790 s for 0% SOC and 50% SOC cells

⁵ Huang, P., Wang, Q, Li, K., Ping, P. & Sun, J. 2014. The combustion behavior of large-scale lithium titanate battery. Scientific Reports 5 : 7788. <https://www.nature.com/articles/srep07788>

respectively. For the 100% SOC cell, it was extinguished with the ejection of the strong smoke flow at 1990 s. the full charged battery combusted more violently than the others.

The state of charge is a critical factor for battery combustion. Comparison between discharged and half-charged cells shows that, the full charged cell is the most hazardous and has a potential threat for the safety. The combustion behaviour of the three 50 Ah LTO batteries is summarized in the following table (Table 2).

Table 2. Summary of three 50 Ah LTO batteries combustion behaviour with different state of charge (adapted from research by Huang et.al.2014).

State of charge (SOC)	0%	50%	100 %
Ignition time [s]	4629	3900	1465
Combustion time [s]	2880	1093	568
Jet fire times	0	1	2
Ignition position	cathode	anode	anode
Anode temperature at ignition [°C]	112	119	121
Maximum flame temperature [°C]	837.3	723.1	747

5. Emissions in battery fire

5.1 Emissions during battery fire (FIOH tests)

The Finnish Institute of Occupational Health, FIOH, is a Finnish research and specialist organization in the field of occupational health and safety. FIOH conducted in 2016 a series of fire tests for Li-ion battery cells (type 515.1740.A, cathode material NMC)⁶. This battery cell type was formerly used in Think⁷ electric car. The tests were conducted in the Emergency Services College⁸ located in Kuopio, Finland. In addition, Metropolia University of Applied Sciences (Helsinki, Finland) was involved in the testing phase. The objective of this research was to identify the quality and quantity of hazardous gases in the smoke produced during a Li-ion battery fire. In addition, the impact of various extinguishing techniques on the emissions from the combustion was studied.

The average concentrations of hydrofluoric and hydrochloric acids measured in the FIOH tests are summarized in Table 3, compared with FIOH and AEGL limit values. A significant amount of hazardous gases was produced during the battery fires. The most significant gases were the emissions of hydrofluoric and hydrochloric acids. In the Finnish occupational

⁶ The FIOH report is available in the internet (in Finnish only):

https://spek.onedu.fi/koulutus/wp-content/uploads/sites/2/2017/12/Loppuraportti-final-1949_001.pdf

⁷ Think! electric car: https://en.wikipedia.org/wiki/Think_City

⁸ The Emergency Services College web-pages: <https://www.pelastusopisto.fi/en/>

safety and health (OSH) recommendations the concentration known to be harmful⁹ for 15 minutes exposure time are for hydrofluoric acid 2,5 mg/m³ and for hydrochloric acid 7,6 mg/m³. Hydrofluoric acid can absorb to human body through the skin, not only through breathing, i.e. lungs. The average emission in the first fire test was 9,2 mg/m³ for hydrofluoric acid and 4,3 mg/m³ for hydrochloric acid. In the second fire test, the average emission was 18 mg/m³ for hydrofluoric acid and 3,5 mg/m³ for hydrochloric acid.

Acute exposure guideline levels¹⁰ (AEGl) 2 and 3 for hydrofluoric acid on 30 minutes exposure time are significantly higher than the concentrations emitted during battery fire tests¹¹. In addition, AEGl values 2 and 3 for hydrochloric acid¹² are much higher than the concentrations reached during battery fire tests. AEGl 1 values on 30 minutes exposure time are lower, but on level 1 the effects are not disabling and are transient and reversible upon cessation of exposure.

Table 3. Average concentrations of hydrofluoric and hydrochloric acids in air during Li-ion battery fire compared to the limit values in different countries

	hydrofluoric acid (= hydrogen fluoride, HF) concentration (mg/m³)	hydrochloric acid (= hydrogen chloride, HCl) concentration (mg/m³)
Burn 1 (FIOH tests)	9,2	4,3
Burn 2 (FIOH tests)	18,0	3,5
Finland: Finnish HTP-values (concentration known to be harmful), max. 15 minutes exposure time	2,5	7,6
AEGl 1 (1 h): Notable discomfort, irritation, or certain asymptomatic non-sensory effects.	0,8 (1 ppm)	2,7 (1,8 ppm)
AEGl 2 (30 min): Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.	28 (34 ppm)	65 (43 ppm)
AEGl 3 (30 min): Life-threatening health effects or death.	51 (62 ppm)	313 (210 ppm)

5.2 Gas emissions from lithium-ion battery fires

In Sweden, Larsson et.al.¹³ have also studied gas and smoke that lithium-ion battery fires generate in addition to heat. They have done some quantitative measurements of heat

⁹ Concentrations known to be harmful: [HTP-arvot 2016](#) (in Finnish).

¹⁰ <https://www.epa.gov/aegl/about-acute-exposure-guideline-levels-aegls>

¹¹ Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 4. Hydrogen Fluoride: Available at: <https://www.ncbi.nlm.nih.gov/books/NBK207733/#ddd00213>

¹² Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 4. Hydrogen Chloride: Available at: <https://www.ncbi.nlm.nih.gov/books/NBK207738/#ddd00124>

¹³ Larsson, F. et.al. 2017. Toxic fluoride gas emissions from lithium-ion battery fires. Scientific Reports volume 7, Article number: 10018. <https://www.nature.com/articles/s41598-017-09784-z>

release and fluoride gas emissions during battery fires for seven different types of commercial lithium-ion batteries (table 4).

Table 4. Details of the tested Li-ion battery cells.

Battery	Number of batteries/test	Battery type	Nominal capacity (Ah)	Nominal voltage (V)	Cell packaging
A	5-10	LCO	6.8	3.75	Prismatic hard Al-can
B	2	LFP	20	3.2	Pouch
C	5	LFP	7	3.2	Pouch
D	9	LFP	3.2	3.2	Cylindrical
E	5	LFP	8	3.2	Cylindrical
F	2	NCA-LATP (LiNiCoAlO ₂ -LiAlTiPO ₄)	30	2.3	Pouch
G	2	Laptop pack	5.6	11,1	Cylindrical

The results show that large amounts of hydrogen fluoride (HF) may be generated, ranging between 20 and 200 mg/Wh of nominal battery energy capacity. In addition, 15–22 mg/Wh of another potentially toxic gas, phosphoryl fluoride (POF₃), was measured in some of the fire tests. Gas emissions when using water mist as extinguishing agent were also investigated.

The measured HF levels indicate that HF can pose a serious toxic threat, especially for large Li-ion batteries and in confined environments. If extrapolated for large battery packs the amounts would be 2–20 kg for a 100 kWh battery system, e.g. an electric vehicle and 20–200 kg for a 1000 kWh battery system, e.g. a small stationary energy storage. The immediate dangerous to life or health (IDLH) level for HF is 0.025 g/m³ (30 ppm) and the lethal 10 minutes HF toxicity value (AEGL-3) is 0.0139 g/m³ (170 ppm). The release of hydrogen fluoride from a Li-ion battery fire can therefore be a severe risk and an even greater risk in confined or semi-confined spaces.

POF₃ was detected only for one of the battery types and only at 0% SOC, showing the complexity of the parameters influencing the gas emission. No POF₃ could be detected in any of the other tests. Using water mist resulted in a temporarily increased production rate of HF, but the application of water mist had no significant effect on the total amount of released HF. Results, as those presented here are crucial to be able to conduct a risk assessment that takes toxic HF gas into account. The results also enable strategies to be investigated for counteractions and safety handling, in order to achieve a high safety level for Li-ion battery applications.

5.3 Comparison of the fire consequences: EV vs. ICE

National Institute of Industrial Environment in France has made a comparison study about the fire consequences of electric vehicle (EV) and internal combustion engine (ICE)¹⁴. In this study, fire tests were achieved for two EV battery units, on a full battery pack, EV with a fully charged battery and for one analogous ICE vehicle (diesel, full tank). In this study, the general behaviour of EV and ICE vehicles were quite similar: the maximal heat release rate, the overall dissipated heat and effective heat of combustion were close to each other in both

¹⁴ Lecocq, A., Bertana, M., Truchot, B. and Marlair, G. 2012. Comparison of the Fire consequences of an Electric Vehicle and an Internal Combustion Engine Vehicle. In: Proceedings from 2nd International Conference on Fires in Vehicles - FIVE 2012, Chicago, USA. SP Technical Research Institute of Sweden. pp. 183-193. ISBN 978-91-87017-54-4. <http://ri.diva-portal.org/smash/get/diva2:962701/FULLTEXT01.pdf>

vehicle types. Also, combustion gases from both vehicle types were quite similar. A significant quantity of HF gases was measured in both EV and ICE fire tests. However, these tests cannot be extrapolated to other vehicles; they are valid only for the vehicles tested during the study.

Another comparative study was accomplished in Japan, where EV and gasoline-powered vehicle fire behaviour were compared with each other in real-scale tests¹⁵. In Japanese tests, Nissan Leaf (EV) and Honda Fit (ICE, petrol engine) were burned. Nissan Leaf had 360 V DC 24 kWh battery fully charged and Honda Fit had 10 litres of gasoline in the tank. Both vehicles were allowed to burn until the fire self-extinguished. Total calculated heat release of the EV was 6.4 GJ and 4.3 GJ for the ICE. The total heat release for ICE was smaller because there were less inflammables in the ICE vehicle. The maximum magnitudes of the heat release rate (EV max. 6.3 MW, ICE max. 2.1 MW) and heat flux for the EV were larger than for the ICE. In these tests, no indications of explosive burn of Li-Ion battery pack were not made.

6. Emergency response guides for electric vehicles

Electric and hybrid car manufacturers have prepared model-specific instructions in cooperation with rescue organizations like National Fire Protection Association in USA. At the moment, there are emergency instructions available for over 35 alternative fuel vehicle manufacturers' products¹⁶, including all major electric car manufacturers and their car models.

6.1 Emergency response guide of Nissan Leaf

In emergency response guide of Nissan Leaf model 2018¹⁷ it is mentioned as follows concerning the vehicle fire:

“Always utilize full Personal Protective Equipment (PPE) and self-contained breathing apparatus during fire fighting operations. Smoke from a LEAF vehicle fire is similar to smoke from a conventional vehicle fire.

In the case of extinguishing a fire with water, large amounts of water from a fire hydrant (if possible) must be used. DO NOT extinguish fire with a small amount of water.

In the event of a small fire, a Type ABC fire extinguisher may be used for an electrical fire caused by wiring harnesses, electrical components, etc. or oil fire. Fire attack should follow standard fire fighting practices.

¹⁵ Watanabe et.al. 2012. Comparison of Fire Behaviors of an electric-battery powered vehicle and gasoline-powered vehicle in a real-scale fire tests. In: Proceedings from 2nd International Conference on Fires in Vehicles - FIVE 2012, Chicago, USA. SP Technical Research Institute of Sweden. pp. 195-205. ISBN 978-91-87017-54-4. <http://ri.diva-portal.org/smash/get/diva2:962701/FULLTEXT01.pdf>

¹⁶ <https://www.nfpa.org/Training-and-Events/By-topic/Alternative-Fuel-Vehicle-Safety-Training/Emergency-Response-Guides>

¹⁷ <https://www.nfpa.org/-/media/Files/Training/AFV/Emergency-Response-Guides/Nissan/Nissan-Leaf-EV-2018---ERG.ashx?la=en>

If you must walk away from the vehicle, notify an appropriate responder or a rescue person of the fact that the vehicle is an electric car and contains a high-voltage system and warn all others.

During overhaul operations (late stage fire suppression process to examine for remaining sources of heat), make sure the battery is fully cooled to avoid fire re-ignition. The battery could reignite if it is placed near fire. To avoid possible electrical shock and serious personal injury, do not breach the high-voltage battery case.”

6.2 Emergency response guide of Tesla Model S

Electric car Tesla model S has suffered from a couple of fire incidents. In some cases, the car has driven over large metal objects at highway speed or hit a concrete wall causing physical damage to the li-ion batteries located in the bottom of the car. The damage on the battery structure has led to short-circuit and thermal runaway of the battery cells and eventually to fire.¹⁸

Tesla Motors has prepared an emergency response guide¹⁹, which is intended only for use by trained and certified rescuers and first responders. About the firefighting in case of battery fire, the emergency guide says as follows:

“If the high voltage battery catches fire, is exposed to high heat, or is bent, twisted, cracked, or breached in any way, use large amounts of water to cool the battery. DO NOT extinguish with a small amount of water. Always establish or request an additional water supply.

Battery fires can take up to 24 hours to extinguish. Consider allowing the battery to burn while protecting exposures.

Use a thermal imaging camera to ensure that the high voltage battery is completely cooled before leaving the incident. The battery must be monitored for at least one hour after it is found to be completely cooled. Smoke or steam indicates that the battery is still heating. Do not release the vehicle to second responders, such as law enforcement and towing personnel, until there has been no heating detected for one hour.

Always advise second responders that there is a risk of battery re-ignition. After Model S has been involved in submersion, fire, or a collision that has compromised the high voltage battery, always store the vehicle in an open area at least 50 ft (15 m) from any exposure.”

Tesla Motors emphasize the importance of the long-lasting extinguishing procedure - lots of water must be used and the battery pack should be monitored for hours in case it heating restarts.

In the Model S emergency guide it is also stated that the burning battery releases toxic vapours and therefore the responders should protect themselves properly against the toxic gases.

¹⁸ Bullis, K. 2013. Are Electric Vehicles a Fire Hazard? MIT Technology review:
<https://www.technologyreview.com/s/521976/are-electric-vehicles-a-fire-hazard/>

¹⁹

https://www.tesla.com/sites/default/files/pdfs/first_responders/2016_Models_S_Emergency_Response_Guide_en.pdf

6.3 Emergency response guide of Honda Clarity

In emergency response guide of Honda Clarity²⁰ (model 2017-2018) it is mentioned as follows concerning the lithium-ion battery fumes or fire.

A damaged high-voltage lithium-ion battery can emit toxic fumes and the organic solvent used as electrolyte is flammable and corrosive, so responders should wear appropriate personal protective equipment. Even after a lithium-ion battery fire appears to have been extinguished, a renewed or delayed fire can occur. The battery manufacturer cautions responders that extinguishing a lithium-ion battery fire will take a large and sustained volume of water.

Responders should always ensure that a Honda Clarity Electric with a damaged battery is kept outdoors and far away from other flammable objects in order to minimize the possibility of collateral fire damage should the battery catch on fire.

7. Firefighting in li-ion battery fire

7.1 Firefighting tactics

7.1.1 U.S. Research

Fire Protection Research Foundation in the U.S. initiated in 2012 a research program to develop best practices where firefighting tactics was one of the main topics. As one result, a research report "Best practices for emergency response to incidents involving electric vehicles battery hazards: A report on Full-Scale testing results"²¹ was published.

Based on the full-scale tests, the following best practices for firefighting tactics and personal protective equipment (PPE) were suggested and observations were made:

- Similar PPE and fire suppression / extinguishing equipment that are used in conventional vehicle fires are appropriate also in fires involving battery-powered vehicles. Any individuals without PPE and Self Contained Breathing Apparatus (SCBA) should remain outside of a 50-foot (~15 metres) radius from the fire. Because of the longer extinguishing time required than in conventional internal combustible engine (ICE) vehicles, there should be either more staff at the site to rotate them or the SCBA cylinders should be able to be switched quickly.
- The use of water does not present an electrical hazard to firefighting personnel. The current PPE is appropriate also with regard to electric shock hazards during non-invasive suppression operations (cutting, piercing etc. operations not included), because during the full scale tests no significant current or voltage readings were indicated in any of the suppression tests.

²⁰ <https://www.nfpa.org/-/media/Files/Training/AFV/Emergency-Response-Guides/Honda/Honda-Clarity-EV-2017-2018-ERG.ashx?la=en>

²¹ Long, R.T., Blum, A.F., Bress, T.J. and Cotts, B.R.T. 2013. Best practices for emergency response to incidents involving electric vehicles battery hazards: A report on Full-Scale testing results. Fire Protection Research Foundation. URL: <https://www.nfpa.org/News-and-Research/Fire-statistics-and-reports/Research-reports/Electrical-safety/Emergency-Response-to-Incident-Involving-Electric-Vehicle-Battery-Hazards>

- Water without any additional additives was able to suppress the fire in every test. The required amount of water increased as the total battery size increased or when the battery was less accessible due to vehicle layout (e.g. a protective battery case). Continuous water flow directly on the battery can shorten time to full extinguishment, but the total amount of water could increase.
- First responders should prepare to suppress the fire at least for an hour or more. In one test the battery reignited 22 hours after the fire was first extinguished. Thermal imaging can be used to monitor the battery cooling process, but it also can provide false security, because the vehicle components and structures and the outer shell of the battery can prevent reliable measurements.
- Damaged or burned Li-ion battery should be stored farther away than 50 feet of any combustible materials until the battery can be safely discharged.
- If a suitable water source is not possible to access and there are no threats to life safety or to nearby combustibles, allowing the battery pack to burn to self-extinguishment may be a viable alternative to suppression. In the tests, the battery pack burned with visibly flame approx. 90 minutes.

If only pure water is used as a suppression agent, the disposed water will not be heavily contaminated; it is slightly more acidic (pH is lower) and contains some chloride and fluoride. No special treatment for the fire suppression water is required.

7.1.2 Extinguishing container for electric cars

A German company Ellermann Eurocon has presented a container called “Red Boxx” for extinguishing of burning electric cars²². After the actual fire, the damaged car can be moved into the waterproof container. The container end can be closed and the container can be filled with 8-10 m³ of water, which cools down the battery pack temperature effectively and prevents the battery fire from re-ignition.

7.1.3 Finnish training material for rescue personnel

Mr. Marko Lauren has published as his B.Sc. thesis²³ a set of training material for rescue personnel in emergencies concerning EVs and hybrid vehicles. In the material, it is emphasized, that in an emergency, the battery pack must not be opened, pierced or cut due to danger of electrical shock and fire.

In the training material, it is said that in case of EV fire any special equipment are not required compared to ICE vehicle battery fire. The personnel shall wear normal firefighting suit and self-contained breathing apparatus. The most effective suppression agent is water, which is needed quite a lot to keep the formation of poisonous gases in minimum. The rescue personnel must be aware of the fact that during the fire, the battery pack can crack and make some small explosions due to heat. The extinguishing of battery fire can be difficult because the cells are usually under protective covers and therefore the suppression agent does not reach the burning cells effectively. It is recommended, that the battery pack should burn to self-extinguishing, is possible.

²² <https://ecomento.de/2017/02/10/dieser-loesch-container-fuer-brennende-elektroautos-macht-es-der-feuerwehr-einfacher/>

²³ Laurén, Marko. 2014. Hybridi- ja sähköautojen koulutusaineisto pelastushenkilökunnalle. Metropolia Ammattikorkeakoulu/Auto- ja kuljetustekniikka. <http://www.theseus.fi/handle/10024/75146> (In Finnish)

7.2 Fire suppression of Li-Ion battery fire

7.2.1 Fire suppression with water

Lithium-ion battery fire suppression is generally recommended to be accomplished mainly with lots of pure water or water-based extinguishing foam. The use of water mist as an extinguishing agent is said to promote the formation of unwanted gases and in the tests conducted in Sweden²⁴ limited measurements show an increase of HF production rate during the application of water mist, but no significant difference in the total amount of HF formed with or without the use of water mist.

There is no risk of electric shock due to battery pack through the water spray/mist according to the tests conducted in the U.S.²⁵ In these tests a 16 kWh Li-ion battery and the test vehicle's interior fire required approx. 4000 litres of water for extinguishing.

In the battery combustion tests conducted in the U.S., water sample from suppression water was collected and sent to laboratory tests. The water sample exhibited a slightly more acidic pH value (7.3) than the control sample collected from the suppression water source. Also low levels of chloride (60 ppm, control: 34 ppm) and fluoride (33 ppm, control: 0,7 ppm) anions were detected. The presence of hydrogen cations increases the acidity of the solution, causing the pH to drop. The concentration of chloride in the sample was only 2 to 3 times greater than normal detected levels, but the concentration of fluoride in the solution was more than 100 times greater than normal detected levels.

7.2.2 The Efficiency of Heptafluoropropane on Suppressing the Lithium Titanate Battery Fire

Wang et.al.²⁶ have studied the efficiency of heptafluoropropane²⁷ (HFC-227ea) on suppressing lithium titanate battery fire. A 50 Ah lithium titanate battery was heated with an electric heater to trigger the thermal runaway. When the battery fire occurred, the heptafluoropropane was immediately discharged by opening the agent storage tank until the fire was extinguished. The temperature of the anode tab rose to approximately 205°C. As soon as the agent was applied, the temperature at anode tab decreased to 65°C within seconds. The flame was controlled completely by the extinguishing agent. The temperatures increased sharply once again at 20 s later, this was because the flammable gases ejected continuously from the cell after the fire was put down and it was reignited.

The results illustrated that the single cell or small-scale lithium titanate battery pack fire can be extinguished by heptafluoropropane in the tests. However, due to the violent reactions still ongoing inner the cell and flammable gases ejecting continuously from the cell, the battery may be reignited after it is put down. Therefore, it was suggested that the heptafluoropropane agent should be applied as early as possible and with longer spray time than the usual case to avoid the reignition.

²⁴ Larsson, F. et.al. 2017. Toxic fluoride gas emissions from lithium-ion battery fires. Scientific Reports volume 7, Article number: 10018. <https://www.nature.com/articles/s41598-017-09784-z>

²⁵ Long, R.T., Blum, A.F., Bress, T.J. and Cotts, B.R.T. 2013. Best practices for emergency response to incidents involving electric vehicles battery hazards: A report on Full-Scale testing results. Fire Protection Research Foundation. URL: <https://www.nfpa.org/News-and-Research/Fire-statistics-and-reports/Research-reports/Electrical-safety/Emergency-Response-to-Incident-Involving-Electric-Vehicle-Battery-Hazards>

²⁶ Wang Q et.al. 2016. The Efficiency of Heptafluoropropane Fire Extinguishing Agent on Suppressing the Lithium Titanate Battery Fire. Fire Technology, 52, 387–396.

<https://link.springer.com/article/10.1007/s10694-015-0531-9>

²⁷ <https://en.wikipedia.org/wiki/1,1,1,2,3,3,3-Heptafluoropropane>

7.2.3 Self-Extinguishing Li-Ion batteries

In the Republic of Korea Yim et. al. have conducted a research²⁸ on fire-extinguishing microcapsules that are embedded into the lithium-ion cell design, into the electrolyte. The idea is that the temperature-responsive micro-capsules release fire extinguisher agent (DMTP (= decafluoro-methoxy-trifluoromethyl-pentane) in PMMA (= polymethyl methacrylate shell)) if the temperature rises over defined temperature.

In the nail penetration test (fully charged stacked-cells with a capacity of 500 mA, the cell assembled with a pristine PE separator showed a drastic temperature increase (72.3 °C) immediately upon the occurrence of an internal short. In contrast, the maximum cell temperature was estimated to be only 37.2 °C for the cell with self-extinguishing microcapsules. The initial temperature of the cells was 25.0 °C.

7.2.4 Aqueous Vermiculite Dispersion (AVD)

In Britannica Academic²⁹ it is stated that vermiculite is a clay mineral and it is typically formed by the alteration of biotite. Large deposits occur in South Africa, Australia, Russia, U.S.A. (South Carolina and Virginia), and Brazil. When rapidly heated to about 300° C, vermiculite can expand to 20 times its original thickness. In its natural state the mineral has little commercial use, but exfoliated vermiculite is extremely light and is used in lightweight concrete or plaster, for thermal and acoustic insulation, or as a packing medium, a soil conditioner, a starting medium for seeds, and a filler or extender in paper, paint, or plastics. In some old vermiculite mines vermiculite has been contaminated with asbestos and using of contaminated vermiculite has caused asbestos-related diseases (e.g. asbestosis)³⁰. New testing methods for identifying asbestos contamination in vermiculite have been introduced, so this should not cause any problems today.

Aqueous Vermiculite Dispersion (AVD) is a fire extinguishing agent suitable for extinguishing small lithium ion battery fires like in mobile phones or in laptop computers. In a suppliers web pages³¹ the principle of vermiculite extinguisher is explained as follows:

“The vermiculite particles within the mist are deposited on the surface of the burning fuel to create a film over the top of the fire. The film instantly dries and because the high aspect ratio platelet particles overlap and bind together, they produce a non-flammable oxygen barrier between the fire and the atmosphere. This process offers a cooling to the surface of the fire and as the AVD platelets begin to build up the layer of vermiculate particles on the top of the fuel source, the fire is gradually cooled and brought under control.”

AVD extinguishing systems are available in different sizes from small portable extinguishers to modular units are available for rapid response units. Also fixed delivery systems are available for high risk environments.

7.2.5 F-500 Encapsulator agent

Hazard Control Technologies Inc. provides F-500 encapsulator agent, which is mentioned to be well suitable for suppressing lithium-ion battery fires³². F-500 reduces the surface tension of water, i.e. makes the water droplets smaller. In smaller droplets the water absorbs heat 6-

²⁸Yim, T et. al. 2015. Self-Extinguishing Lithium Ion Batteries Based on Internally Embedded Fire-Extinguishing Microcapsules with Temperature-Responsiveness. NanoLetters, American Chemical Society. Available: <https://pubs.acs.org/doi/abs/10.1021/acs.nanolett.5b01167>

²⁹ <https://academic.eb.com/levels/collegiate/article/vermiculite/75114>

³⁰ https://en.wikipedia.org/wiki/Vermiculite#Asbestos_contamination

³¹ Dupré Minerals Limited, England: <https://www.avdfire.com/>.

³² <http://www.hct-world.com/industry-applications/industry/automotive/>

10 better than pure water and penetrates better to the material in fire. The recommended proportion in water in case of lithium-ion battery fire is 3%. According to the materials found on the manufacturer's website³³, Dekra, Daimler and Deutsche ACCUmotive also tested agents on lithium-ion battery fires and concluded F-500 EA was the recommended agent to extinguish hybrid and electric vehicle fires. F-500 EA is noncorrosive, nontoxic and biodegradable extinguishing agent.

8. Conclusions and ideas for further research

The most common way to deal with Li-Ion battery fire is to extinguish and cool it down with a significant amount of water. In addition, chemical suppression agents can be used to suppress the flames in the beginning of the fire for a while, but the cooling must be still done with water, in other case the battery will self-ignite again. In underground solutions, it is not an ideal option to allow the battery pack burn to self-extinguishment because of the rock integrity decreases due to heat and because of the loss of production as the all underground operations should be stopped in the case of battery fire.

There were no indications in any emergency guides or research papers that there might be danger of electrical shock for the firefighters while the battery pack is extinguished with water. However, it is advisable to make an occupational risk analysis of the battery pack fire extinguishing work to ensure that there is no risks of electrical shocks. Touching the vehicle equipped with damaged li-ion battery or the damaged battery pack itself can be dangerous.

As one of the main goals in firefighting against battery pack fire is to decrease the temperature of the battery pack, the emergency situation should be taken into account in the battery pack design. The work machine batteries could weigh several tons and therefore cooling only from the outer parts could be ineffective. If possible, the battery pack should be designed in a way that makes it possible to cool the pack also from the inside, maybe by utilising the existing cooling channels used for the battery pack temperature management. Also an extinguishing container type of strategy can be applied onboard a machine; the waterproof outer shell of the battery pack can be filled with cold water in case of battery fire to cool the cells down. The battery shell can be equipped with connectors to e.g. mine's fresh water system to speed up the starting of the cooling process. This strategy could also significantly decrease the amount of the water needed for the extinguishing.

Even though the battery packs might be similar modules in different machines, the machine structure is always machine model specific. To ease the work of the first responders, machine type specific instructions should be prepared. The instructions should be based on a structured, analytical approach where the whole scenario from the identification of the ignition sources to full suppression are analysed. The instructions should also contain aid for the operators to identify the battery event; all electric work machine fires are not necessarily caused by batteries.

The conventional personal protective equipment (including Self Contained Breathing Apparatus, SCBA) used by rescue personnel in ICE car fires should be effective enough also in the case of EV battery fire, even if there might exist considerable amount of HF and HCl gases in the site of fire. It might be worth consideration to wear suits that have higher water vapour resistance (level Z1³⁴) to prevent the fumes entering through the skin. This topic should be studied more further especially from the underground operations point of view where the concentrations of toxic compounds in air in case of Li-Ion battery fire can be much

³³ http://www.hct-world.com/wp-content/uploads/2013/06/CH_F5_AUT_Chronology-Fire-Suppression-for-Hybrid-and-Electric-Vehicles_V2.pdf

³⁴ EN 469:2005. Protective clothing for firefighters. Performance requirements for protective clothing for firefighting.

higher than in open air. This does not only concern mining applications, e.g. electric car fire in an underground parking garage requires similar personal protective equipment.

As the working personnel in underground workplaces like mines cannot always carry such heavy PP equipment with them, they should be equipped with PPE effective enough to move away from the fire to the rescue chamber or similar safe location. There are breathing masks available in the market that can filter HF gases, but there are some aspects that should be studied: For example, are they effective enough in case of li-ion battery fire underground and are they usable against all gases the variety of lithium-ion battery chemicals can emit during fire. There are also escape hoods that can provide constant air supply for several minutes from a gas container; they are probably more usable for escaping away from the burning machine in the case of battery fire.